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(54) **Poly(Carboxylic Acid)
Hardenable Compositions**

(57) Hardenable compositions exhibiting high transverse strength are prepared by mixing a poly(carboxylic acid) or a hydrolysable precursor thereof, particularly polyacrylic acid, with a particulate, ion-leachable material, particularly a silicate, aluminosilicate or fluoraluminosilicate, especially as a powdered glass, in the

presence of water and a filler the particles of which have a high flexural modulus and are anisotropically dimensioned (e.g. as in fibres, acicular or columnar crystals, and flakes). Suitable fillers include metals, alloys, refractories, glass fibres, carbon fibres, and polyalkylene fibres. The cements so formed find application particularly, but not exclusively, in dentistry, for example as a dental amalgam replacement.

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SPECIFICATION

Hardenable Compositions

This invention relates to hardenable compositions; more particularly, this invention relates to such compositions containing a polymeric component which comprises a water-soluble polymer of one or more unsaturated mono- or poly-carboxylic acids (hereinafter referred to as a "poly(carboxylic acid)"). The invention finds particular, but not exclusive, application in the dental material art and will be hereinafter described, without prejudice to its generality, with particular reference to that art.

Dental amalgam (which is an extemporaneously compounded amalgam of mercury with the intermetallic phase Ag_3Sn) has proved to be a very satisfactory material for posterior oral restorative work notably on account of its very good mechanical properties, such as compressive strength and hydrolytic stability. Nonetheless it has several serious disadvantages: thus, it does not adhere to freshly-cut dentine nor does it provide in situ resistance against caries; it provides no resistance to thermal shock thereby necessitating the provision of an intermediate insulating cavity liner; and it initially provides a poor seal at the margins thereby permitting marginal percolation and concomitant secondary caries to occur.

Perhaps dental amalgam's gravest disadvantage is in its containing mercury, the toxicity of which has made it notorious. While no connection has yet been established between amalgam dental fillings and ill-health in patients (although enamel surrounding such fillings in time becomes stained black, presumably due to migration of metal ions), mercury has proved to be a hazard to the dental technician or assistant who triturates the material in a mortar. Thus, surveys have shown that they take in mercury by inhalation or by absorption through the skin, and that the mercury content of their blood is frequently high; indeed, a small number of cases of fatal mercury poisoning have been recorded.

It is manifestly desirable that an alternative material, free from mercury, is developed, particularly when the likelihood of increasingly stringent health legislation and the increasing scarcity on mercury are considered. This invention provides such a replacement material.

According to the present invention, there is provided a hardenable composition comprising:

- (i) a poly(carboxylic acid) or a hydrolysable precursor thereof;
- (ii) a particulate ion-leachable material; and
- (iii) a filler, different from (ii), the particles of which have a high flexural modulus and are anisotropically dimensioned, (ii) being reactible with (i) in the presence of water to form a cement.

By "high flexural modulus" in (iii) is meant a flexural modulus which is at least that of the cement matrix formed by reacting (ii) with (i). This will generally be greater than 20 GPa, suitably greater than 30 GPa, and preferably very much greater, for example from 75 GPa to 400 GPa.

By "anisotropically dimensioned" in (iii) is meant that the particle has one dimension differing substantially from the others; for example, the length of a fibre or acicular or columnar crystal or the thickness of metal flake.

It is envisaged that (iii) may comprise metals or high modulus inorganic or organic materials.

Examples of metals suitable as such for use as (iii) include aluminium, chromium, cobalt, copper, indium, iron, nickel, silver, tin, titanium, tungsten or zinc; alloys thereof, for example, copper-tin alloys, gold-indium alloys, gold-tin alloys, gold-zinc alloys, nickel-aluminium alloys, cobalt-chromium alloys, nickel-chromium alloys, nickel-titanium alloys, stainless and other steels, silver-tin alloys; intermetallics, such as NiAl and Ag_3Sn , preferably Ag_3Sn , are particularly preferred.

Mixtures of particulate metal may be particularly desirable, in the dental material art, where one such metal (for example Ag_3Sn) imparts strength to the cement while the other, more ductile such metal (for example dental gold) imparts burnishability and improved appearance.

Particularly preferred metals are fibrous metals spun from the melt, particularly by melt extraction techniques.

Examples of high modulus inorganic or organic materials suitable for use as (iii) include fibrous refractory oxides, nitrides or carbides, or glass fibres; or carbon fibres or polyalkylene fibres. Specific examples are alkali metal titanates, for example potassium titanate, alumina, carburised tungsten wire, glass, silica, silicon carbide, silicon (oxy)nitride, titanium nitride and zirconia, all in fibrous form; carbon fibres and high modulus homo- and co-polyalkylenes (for example as disclosed in UK 1469526, 1498628, 1506565, 45920/75 and 7919737). Particularly preferred such materials are glass fibres reactible with (i) in the presence of water to form a cement, and carbon fibre.

Where the metals (for example gold, platinum or rhodium) or the high modulus inorganic or organic materials are not reactive with (i) and it is desirable that the bonding to the cement matrix is enhanced, it may be coated with a metal or metal oxide which does so react. Examples of such coatings include indium, iron, nickel, tin, zinc or an oxide thereof.

In order to attain a cement which has high transverse strength typically greater than 20 MPa when measured in accordance with BS5199:1975, it is found advantageous to ensure that at least 50% by weight, preferably 60% to 90%, of (iii) is in the form of rod-shaped particles. Suitably, such particles have a length: thickness ratio of at least 4:1. Desirably, for dental applications, the mean length will be no more than about 1 mm while the mean thickness will be from $10\text{ }\mu\text{m}$ to $200\text{ }\mu\text{m}$, preferably less than $50\text{ }\mu\text{m}$, though larger particles may be used in other applications.

Suitably (iii) is present in an amount of up to 50% volume fraction preferably 20% to 40%, especially 25% to 30%, based on the weight of (ii). Desirably, the powder:liquid ratio of (ii) to (i), the latter being present as a 50% by weight aqueous solution, is from 0.8 to 4.5 (g/ml), preferably 1.3 to 2.0 (g/ml). Typical volume fractions of (iii):(ii):(i) are about 25%:25%:50% (in weight fraction terms 5 66%:18%:16%).

However, where (iii) is also a particulate, ion-leachable material, for example a fluoroaluminosilicate glass fibre, reactible with (i) in the presence of water, the amount of (iii) may be substantially higher replacing a part of all of (ii).

It is highly desirable that (iii) should be readily wettable by (i) to ensure a homogeneous mix; 10 surface treatment of (iii), such as etching and/or oxidation, may facilitate this.

The preferred poly(carboxylic acids) suitable for use as (i) are those prepared by the homopolymerisation and copolymerisation of unsaturated aliphatic carboxylic acids for example aconitic acid, acrylic acid, citraconic acid, fumaric acid, glutaconic acid, itaconic acid, maleic acid, mesaconic acid, methacrylic acid, muconic acid and tiglic acid; and the copolymerisation of these acids 15 with other unsaturated aliphatic monomers for example vinyl monomers, such as vinyl hydrocarbon monomers, vinyl ethers, acrylamide or acrylonitrile. Particularly preferred are the homopolymers of acrylic acid and its copolymers, particularly copolymers of acrylic acid and itaconic acid, especially those described and claimed in UK 1484454. Good results have also been obtained using a copolymer of vinyl methyl ether and maleic acid.

It is also possible to use a hydrolysable precursor of a poly(carboxylic acid) as (i); as used in this specification, "hydrolysable precursor" means a polymer which will be transformed into the poly(carboxylic acid) on hydrolysis, for example a poly(carboxylic acid anhydride); furthermore, polyacrylic acids may be prepared by hydrolysis of corresponding polyacrylonitriles. The hydrolysable precursor of a poly(carboxylic acid) may be a homopolymer of an unsaturated carboxylic acid 20 anhydride or a copolymer with an above mentioned other carboxylic acid or anhydride thereof; or a copolymer of an unsaturated carboxylic acid anhydride with an unsaturated aliphatic monomer, for example vinyl monomers, such as vinyl hydrocarbon monomers, vinyl ethers, acrylamide or acrylonitrile. Good results may be obtained by using homopolymers of maleic anhydride or vinyl orthophthalic anhydride, or copolymers thereof, especially block copolymers thereof, with ethylene, 30 propylene, butenes, styrene and vinyl methyl ether.

The poly(carboxylic acid) or hydrolysable precursor thereof is preferably linear, although branched polymers may also be used. Preferably the polymer has an average molecular weight from 1,000 to 1,000,000, more preferably from 1,000 to 250,000, and most preferably from 5,000 to 100,000, especially from 10,000 to 25,000. In this specification the average molecular weight is defined as 35 being that measured by ultracentrifuging.

The preferred components (ii) are aluminosilicates or fluoroaluminosilicates, particularly glasses thereof, wherein the ratio by weight of acidic to basic oxides in the glass is such that the glass will react with (i) in the presence of water and, desirably, a water-soluble complexing agent, for example a water-soluble chelating agent such as tartaric, citric or mellitic acid, to set to a hardened composition. The 40 principal acidic oxide in the glass is a silica, although the glass may also contain minor amounts of other anhydrides such as phosphorus pentoxide and boric oxide. The principal basic oxide in the glass is alumina which, although it has amphoteric properties, can be considered for the purposes of the present invention solely as a basic oxide. Particularly preferred glasses fall within the composition range of 10 to 65% w/w silica and 15 to 50% w/w alumina.

The glass desirably contains at least one other basic oxide, preferably calcium oxide, which may be present in the glass composition in an amount from 0 to 50% w/w. The calcium oxide may be partly or wholly replaced by sodium oxide or other basic oxide or a mixture of basic oxides, although in some applications the presence of sodium oxide may be undesirable as this oxide tends to increase the solubility of the resulting cement. Preferred glasses for use in the present invention containing alumina, 50 silica and calcium oxide are the gehlenite and anorthite glasses, and in general glasses falling within the composition range 10 to 65% w/w silica, 15 to 50% w/w alumina and 0 to 50% w/w calcium oxide.

Other glasses suitable for use in the present invention may contain fluoride, suitably up to 15% by weight, preferably less than 10% by weight. A class of fluoroaluminosilicate glasses particularly suited 55 to dental applications are those wherein the ratio by weight of silica to alumina is from 1.5 to 2.0 and the ratio by weight of silica to alumina is from 0.5 to 1.5 and the ratio by weight of fluorine to alumina is from 0.25 to 2.0.

The glasses suitable for use in the present invention may be prepared by fusing mixtures of the components in the appropriate proportions at temperatures above 900°C and preferably in the range 60 of 1050°C to 1550°C. The mixture is preferably fused from 1 to 4 hours. Silica and alumina may be included in the mixture as oxides, though it is convenient to add calcium oxide and sodium oxide as calcium carbonate and sodium carbonate respectively, and reference to the presence of these oxides in a glass fusing mixture includes the possibilities that they may be added as carbonates or as other compounds which decompose similarly under glass fusion conditions to give the oxides.

The addition of carbonates to the fusion mixture lowers the fusion temperature and thus these can 65

be considered as fluxing agents. If desired, however, the mixture may contain an additional fluxing agent, and this has been found to be important with glass compositions containing less than 10% w/w of calcium oxide. In this connection, fluorides such as fluoride and cryolite have been found to be especially useful as fluxing agents, although it is desirable not to use large amounts of fluorides in the fusion mixture. Other fluxing agents, for example calcium phosphate and aluminium phosphate may also be used. The total amount of fluxing agents present in the mixture, including carbonates, may be up to 50% by weight, based on the total weight of mixture.

After fusion the glass may be poured off and cooled rapidly, for example, in air or water or some combination of both. To a first approximation the proportions of the different elements in the glass may be taken as the proportions of the same elements present in the mixture. Some fluorine may, however, be lost from the fluoride fluxing agent during the reaction.

Glasses used in the present invention may be readily obtained in fine powder form. The degree of fineness of the powder should preferably be such that it produces a smooth cement paste which sets within an acceptable period when mixed with the poly(carboxylic acid) in the presence of water. Preferably the degree of fineness of the powder is such that it will pass through a 150 mesh B.S. sieve and most preferably such that it will pass through a 350 mesh B.S. sieve. Mixtures of different glasses may be used if desired.

The silicate may also be a naturally-occurring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having an Al:Si molar ratio greater than 2:3, or blast furnace slags; or Portland cement. Examples of such materials include aphrosiderite, danalite, gehlenite, hemimorphite, larnite, levynite, nepheline, muscovite, sodalite, scolecite, spurrite, thuringite, willemite, wollastonite (including calcined wollastonite).

The hardenable composition of the invention may be stored in any suitable manner providing that means are provided to prevent premature reaction of the components (ii) (and where possible (iii)) with (i) in the presence of water. Thus, the composition may be stored as a dry powder, suitably comprising an intimate mixture of the poly(carboxylic acid) or hydrolysable precursor thereof (i) in particulate form with (ii) and (iii). Alternatively, an aqueous solution of (i) can be dried on to (iii) which is then powdered and blended with (ii). In many cases, however, it is found that mixing is improved by using the poly(carboxylic acid) (i) in the form of an aqueous solution, which may contain from 20 to 65% by weight of the poly(carboxylic acid). Where this is done, (iii) may be included in admixture with (ii) or be separate therefrom. Furthermore, any water-soluble complexing agent present may be included with one or more of (i), (ii) or (iii) in an amount from 0.01% to 30% by weight of (i).

The hardenable compositions of this invention may be used as dental cements for use as filling materials for restoring posterior teeth. They may also be formed as hardenable sheet materials, for example by depositing the components, optionally in intimate admixture, upon a flexible support web which may be woven, laid down as a non-woven fabric, cast or extruded. The hardenable compositions may also be used in the building industry as surface coatings, flooring materials, speciality cements, including groutings, panellings, shuttering and adhesives. They may also be used to seal exposed and hazardous asbestos surfaces and claddings.

The following Example illustrates the invention.

Example

A variety of fillers, all of which had particles which were anisotropically dimensioned, was premixed with a glass powder; and this premix was then mixed with an aqueous polyacid. Details are shown in the Table below. In every case both the glass powder and the aqueous polyacid were as marketed under the registered Trade Mark "Chembond".

The mixture was then moulded into a test specimen and its transverse strength was tested as described in BS. 5199:1975 save that the mould dimensions were 25×3×3 mm.

Table

| | <i>Filler:Glass Premix Weight Ratio</i> | <i>Solid:Liquid Mix Weight Ratio</i> | <i>Liquid Weight</i> | <i>Mean Transverse Strength (MPa)</i> | |
|---|---|--|--------------------------|---|----|
| 50 | | | | | 50 |
| Filler | | | | | |
| Silica fibre ¹ | 1:2 | 2.3:1 | 0.5 g | 25.9 | |
| Glass fibre ² | 1:2 | 1.9:1 | 0.6 g | 20.6 | |
| Titanium ³ | 1:1 | 2.3:1 | 0.5 g | 18.2 | |
| 55 | | | | | 55 |
| Titanium (oxidised at 450°C for 15 mins) | 1:1 | 2.8:1 | 0.5 g | 20.6 | |
| Titanium (etched in Tucker's etch) | 1:1 | 2.3:1 | 0.5 g | 22.0 | |
| 60 | | | | | 60 |
| Titanium (etched and oxidised) | 1:1 | 2.3:1 | 0.5 g | 22.4 | |
| NiAl ⁴ (intermetallic compound) | 2:1 | 4.6:1 | 0.5 g | 22.0 | |

Table (cont.)

| Filler | Filler:Glass | Solid:Liquid | Liquid | Mean | |
|--------|---|--------------|--------|----------------|----|
| | Premix Weight | Mix Weight | | | |
| | Ratio | Ratio | Weight | Transverse | |
| | | | | Strength (MPa) | |
| 5 | Aluminium ⁶ | 1.67:1 | 0.5 g | 21.4 | 5 |
| | Glass Fibre ⁸ | 1.4:1 | 0.7 g | 30.1 | |
| | Chromium ⁷ | 2.3:1 | 1.0 g | 21.5 | |
| | Ag ₃ Sn ⁸ | 4.5:1 | 1.0 g | 40.0 | |
| | Carbon fibre ⁹ | 1:4 | 1.0 g | 43.0 | |
| 10 | | | | (66.0 max.) | 10 |
| | Carbon fibre ⁹ | 1:4 | 1.0 g | 46.7 | |
| | Carbon fibre ⁹ | 1:4 | 1.0 g | 53.0 | |
| | Carbon fibre ⁹ | 1:4 | 1.0 g | 53.0 | |
| | Carbon fibre ⁹ | 1:4 | 1.0 g | 53.0 | |
| 15 | Al ₂ O ₃ ¹⁰ | 1:3 | 1.0 g | 44.3 | 15 |
| | Al ₂ O ₃ ¹⁰ | 1:2 | 1.0 g | 21.9 | |
| | 1. Sold as a woven tape by the Chemical and Insulating Co. Ltd., under the trade mark "Refrasil". | | | | |
| | 2. A Pb-free glass wool, ex British Drug Houses Ltd. | | | | |
| 20 | 3. Ti powder 8996-3 stated to be >99.5% Ti ex Koch-Light Ltd., <45 μ fraction was sieved out and used in the experiment. | | | | |
| | 4. Machined to provide chips which are then ball-milled to give acicular particles. | | | | |
| | 5. Atomised Al 8201-30 stated to be >99.98% Al ex Koch-Light Ltd. <45 μ fraction was sieved out and used in the experiment. | | | | |
| 25 | 6. A glass of the formula: SiO ₂ 175 pts. wt; Al ₂ O ₃ 100; Na ₃ AlF ₆ 93; CaF ₂ 113; AlF ₃ 82; AlPO ₄ 60. | | | | |
| | 7. Ball-milled electrolytic chromium of high purity ex Murex Ltd. | | | | |
| | 8. Prepared by melt extraction. | | | | |
| | 9. Ex Courtaulds designated Grafil-AS; random chopped. | | | | |
| 30 | Ex Toray designated: Torayca T300—1000. | | | | |
| | Ex Courtaulds designated: Grafil-A. | | | | |
| | Ex Courtaulds designated: Grafil-HM-S. | | | | |
| | Ex Thornel | | | | |
| | 10. Fibre ex I.C.I. Ltd., designated "Saffil". | | | | |
| 35 | By comparison, a control free from filler gave a value for transverse strength of 10 MPa. A sample of Ag ₃ Sn in which the particles were essentially spherical gave, under an identical test to 8, a value for transverse strength of only 13 MPa. | | | | |
| | 35 | | | | |
| | Claims | | | | |
| | 1. A hardenable composition comprising: | | | | |
| 40 | (i) a poly(carboxylic acid) or a hydrolysable precursor thereof; | | | | |
| | (ii) a particulate, ion-leachable material; and | | | | |
| | (iii) a filler, different from (ii), the particles of which have a high flexural modulus and are anisotropically dimensioned, (ii) being reactible with (i) in the presence of water to form a cement. | | | | |
| | 2. A composition according to Claim 1 where (iii) has a flexural modulus greater than 30 GPa. | | | | |
| 45 | 3. A composition according to Claim 1 or 2 wherein (iii) comprises a metal. | | | | |
| | 4. A composition according to Claim 3 wherein (iii) comprises aluminium, chromium, cobalt, copper, indium, iron, nickel, silver, tin, titanium, tungsten or zinc; a cobalt-chromium alloy, a copper-tin alloy, a gold-indium alloy, a gold-tin alloy, a gold-zinc alloy, a nickel-aluminium alloy, a nickel-chromium alloy, a nickel-titanium alloy, a stainless or other steel, a silver-tin alloy; NiAl and Ag ₃ Sn. | | | | |
| 50 | 5. A composition according to Claim 3 or 4 where (iii) is in fibrous form. | | | | |
| | 6. A composition according to Claim 4 or 5 wherein (iii) comprises Ag ₃ Sn. | | | | |
| | 7. A composition according to any preceding claim wherein (iii) comprises a fibrous refractory oxide, nitride or carbide, or a glass fibre. | | | | |
| 55 | 8. A composition according to Claim 7 wherein the glass fibre is reactible with (i) in the presence of water to form a cement. | | | | |
| | 9. A composition according to any preceding claim wherein (iii) comprises carbon fibre or polyalkylene fibre. | | | | |
| | 10. A composition according to any preceding claim wherein the particles of (iii) are coated with a metal or metal oxide reactable with (i). | | | | |
| 60 | 11. A composition according to any preceding claim wherein at least 50% by weight of the particles of (iii) are rod-shaped. | | | | |

12. A composition according to Claim 11 wherein such particles have a length:thickness ratio of at least 4:1.
13. A composition according to any preceding claim wherein (iii) is present in an amount of up to 50% volume fraction, based on the weight of (ii).
- 5 14. A composition according to Claim 8 wherein (ii) is present in an amount greater than 50% volume fraction, based on the weight of (ii). 5
15. A hardenable composition comprising:
(i) a poly(carboxylic acid) or a hydrolysable precursor thereof; and
(ii) an ion-leachable material, the particles of which have a high flexural modulus and are
10 anisotropically dimensioned, 10
(ii) being reactible with (i) in the presence of water to form a cement.
16. A composition according to any preceding claim wherein (i) comprises polyacrylic acid or a copolymer of acrylic acid with aconitic acid, acrylic acid, citraconic acid, fumaric acid, glutaconic acid, itaconic acid, maleic acid, mesaconic acid, methacrylic acid, muconic acid or tiglic acid, or a
15 hydrolyable precursor thereof. 15
17. A composition according to any preceding claim wherein (i) has an average molecular weight from 10,000 to 100,000.
18. A composition according to any preceding claim wherein (i) is present in aqueous solution in an amount of up to 50% by weight.
- 20 19. A composition according to any preceding claim wherein (ii) is an aluminosilicate or fluoraluminosilicate glass. 20
20. A cement prepared from a composition according to any preceding claim and having a transverse strength greater than 20 MPa.
21. A cement according to Claim 20 which has a transverse strength greater than 30 MPa.